

AD-A182 481

STUDY OF THE OXIDATION STATE OF COPPER IN LA18SR2CU04  
(U) BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY  
Y ZHANG ET AL 05 JUN 87 TR-8 N00014-86-K-0234

1/1

UNCLASSIFIED

F/G 20/5

NL

END  
8-87  
DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A182 401

12

OFFICE OF NAVAL RESEARCH

CONTRACT No. N000 14 86K0234

TECHNICAL REPORT No. 8

DTIC FILE COPY

STUDY OF THE OXIDATION STATE OF COPPER IN  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$

by

Y-C. Zhang, J-H. Liu, K. Dwight, P. H. Rieger and A. Wold

Prepared for publication  
in  
SOLID STATE COMMUNICATIONS

Brown University  
Chemistry Department  
Providence, Rhode Island 02912

DTIC  
ELECTE  
JUL 15 1987  
S D  
G D

June 5, 1987

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release and sale;  
its distribution is unlimited

67

ADA182401

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT <b>APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED</b>	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) <b># 8</b>			5. MONITORING ORGANIZATION REPORT NUMBER(S) <b>NOO0 14 86K0234</b>	
6a. NAME OF PERFORMING ORGANIZATION <b>AARON WOLD BROWN UNIVERSITY</b>		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION <b>OFFICE OF NAVAL RESEARCH DR. DAVID NELSON</b>	
6c. ADDRESS (City, State, and ZIP Code) <b>CHEMISTRY DEPARTMENT, BOX D PROVIDENCE, RI 02912</b>			7b. ADDRESS (City, State, and ZIP Code) <b>CODE 472 800 N. QUINCY STREET ARLINGTON, VA 22217</b>	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO	
			PROJECT NO	
			TASK NO	
			WORK UNIT NO	
11. TITLE (Include Security Classification) <b>STUDY OF THE OXIDATION STATE OF COPPER IN <math>\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4</math></b>				
12. PERSONAL AUTHOR(S) <b>Y-C. Zhang, J-H. Liu, K. Dwight, P. H. Rieger and A. Wold</b>				
13a. TYPE OF REPORT <b>Technical</b>		13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) <b>June 5, 1987</b>	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION <b>PREPARED FOR PUBLICATION IN SOLID STATE COMMUNICATIONS</b>				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <b>Samples of <math>\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4</math> were prepared by decomposition of the nitrates. From magnetic susceptibility, temperature programmed reduction and ESR measurements, it is concluded that the Cu(II) has most probably disproportionated to Cu(I), Cu(III).</b> <i>(Keyed in from the nitrate, lanthanum, strontium)</i>				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> FOR USERS			21. ABSTRACT SECURITY CLASSIFICATION	
22. NAME OF DISTRIBUTION / AVAILABILITY			23. NAME OF SECURITY / AVAILABILITY	

DL/1113/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 92132	1

Accession	
DTIC	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
DTIC	Unpublished <input type="checkbox"/>
by	
Date	
Availability Codes	
Available for special	
A-1	

STUDY OF THE OXIDATION STATE OF COPPER IN  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$

Y-C. Zhang, J-H. Liu, K. Dwight, P. H. Rieger and A. Wold\*

Chemistry Department, Brown University,  
Providence, Rhode Island 02912

\*Address all correspondence

(Received 21 May 1987 by J. Tauc)

Samples of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  were prepared by decomposition of the nitrates. From magnetic susceptibility, temperature programmed reduction and ESR measurements it is concluded that the Cu(II) has most probably disproportionated to Cu(I), Cu(III).

## Introduction

In the last few months the compound  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  has received much attention in the literature because of its high temperature superconducting transition. This compound was reported to have a superconducting transition at 36K (1-4). X-ray data from both powder diffraction and single crystals indicated that this compound has an undistorted tetragonal  $\text{K}_2\text{NiF}_4$  type structure (1,2,5). A single crystal study has indicated that the compound crystallizes in the space group of  $I4/mmm$  (5). The coordination geometry around the copper atoms is a tetragonally elongated octahedron with four short copper-oxygen bonds  $d[\text{Cu-O}(1)] = 1.90\text{\AA}$ , and two long bonds  $d[\text{Cu-O}(2)] = 2.41\text{\AA}$ . The high temperature superconducting transition has been attributed to the existence of mixed oxidation states of copper in the structure (1,3), but the valence and valence distribution of copper in the compound have not been determined. The oxidation state of copper in  $\text{Ba}_2\text{YCu}_3\text{O}_x$  has a crucial effect on the superconducting transition of the compound as demonstrated by a recent, careful study (6). Therefore, the determination of copper valence in  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  could be a key for the understanding of the superconducting mechanism of the compound. It is the purpose of this work to study the oxidation state of copper in the  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  structure.

## Experimental

Samples of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  were prepared by codecomposition of the corresponding nitrates. The starting compounds were high purity copper metal (Matthey S. 50250),  $\text{La}_2\text{O}_3$  (Lindsay #528 99.999%), and  $\text{SrCO}_3$  (Matthey 2H118, 99.999%). The copper was prereduced in 85%Ar/15% $\text{H}_2$  at 450°C for 6 hours. The  $\text{La}_2\text{O}_3$  was heated at 800°C for 8 hours to drive off adsorbed  $\text{CO}_2$  and water. The molecular weight of the  $\text{SrCO}_3$  was analyzed as 147.6 by thermogravimetric analysis. A mixture of 254.2 mg copper metal, 1172.9 mg  $\text{La}_2\text{O}_3$  and 118.1 mg  $\text{SrCO}_3$  was dissolved in 6 ml of concentrated nitric acid to convert all of the initial compounds to nitrates. The solution was dried at 150°C for 12 hours and then predecomposed at 500°C for 4 hours. The sample was ground and heated at 970°C for 120 hours. During the heating the sample was taken out and ground 4 times. Finally, the sample was quenched to room temperature by taking it out of the furnace at

the elevated temperature. The sample of pure  $\text{La}_2\text{CuO}_4$  was prepared by the same procedure.

#### Characterization of products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.5405\text{\AA}$ ). The diffraction patterns were taken in the range  $12^\circ < 2\theta < 75^\circ$  with a scan rate of  $1^\circ 2\theta/\text{min}$  and a chart speed of 30 in/hr.

Temperature programmed reduction of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  was carried out using a Cahn System 113 thermal balance. The sample was purged in a stream of 85%Ar/15%H<sub>2</sub> for 2 hours. Then the temperature was increased to 990°C at a rate of 50°/hr. The flow rate of the gas mixture was 60 ml/min.

Magnetic susceptibility measurements were carried out using a Faraday Balance (7) from 77 to 300K with a field strength of 10.4kOe. Honda-Owen (field dependency) measurements were carried out at both 77 and 296K.

Electron spin resonance spectra of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and  $\text{La}_2\text{CuO}_4$  were recorded using a Bruker ER220D Spectrometer at room temperature. The frequency was  $\nu_0 = 9.464\text{ GHz}$ , the microwave power was 200 mW, and the field modulation amplitude was 1 Gauss.

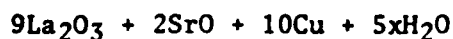
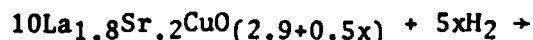
#### Results and Discussion

The x-ray powder diffraction patterns of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  are given in Fig. 1(a) and (b).  $\text{La}_2\text{CuO}_4$  shows a single phase which can be indexed on the basis of a distorted  $\text{K}_2\text{NiF}_4$  type structure. The data obtained is consistent with those of orthorhombic  $\text{La}_2\text{CuO}_4$  reported by J. M. Longo (8).  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  was also prepared as a single phase and could be indexed on the basis of an undistorted tetragonal  $\text{K}_2\text{NiF}_4$  type structure. The tetragonal phase is the superconducting phase with a transition reported to be about 36K (1-3).

The average oxidation state of copper in the  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  was determined from the TPR results shown in Fig. 2. X-ray diffraction confirmed that that  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  decomposed completely during the reduction, the detectable reduction products being  $\text{La}_2\text{O}_3$  and metallic copper (Fig. 1(c)). The reduction proceeded



according to the following equation:



where  $x$  is the average oxidation state of the copper ions. From the ratio of final and initial weights the average valence of the copper ions was determined as  $2.00(\pm 0.04)$ . There are several possibilities consistent with these results. The copper could remain all  $\text{Cu}^{2+}$ , disproportionate to  $\text{Cu}^+$  and  $\text{Cu}^{3+}$ , or be a mixture of all three valencies. In order to help determine the most probable oxidation state, an Electron Spin Resonance study was carried out.

In the  $\text{La}_2\text{CuO}_4$  structure, the Cu ion has an elongated octahedral coordination with respect to oxygen (3,8). The lengths of the four short planar Cu-O bonds are 1.90Å, and the two long Cu-O bonds along the  $+z$  and  $-z$  direction are 2.43Å. Hence, the copper is actually in a square planar coordination with respect to oxygen. Wang et al. have reported that  $\text{La}_{1.85}\text{Sr}_{.15}\text{CuO}_4$  has a tetragonal  $\text{K}_2\text{NiF}_4$  structure with space group  $\text{I}4/\text{mmm}$ . The four short  $[\text{Cu}-\text{O}(1)]$  bonds and the two long  $[\text{Cu}-\text{O}(2)]$  bonds are 1.90Å and 2.41Å, respectively (5). They found that copper ions were also in a tetragonally distorted octahedral site. The copper ions in  $\text{La}_{1.85}\text{Sr}_{.15}\text{CuO}_4$  are also primarily square planar coordinated with respect to oxygen. Since there is an apparent structural similarity of Cu in the two compounds,  $\text{Cu}^{2+}$  in  $\text{La}_2\text{CuO}_4$  can be used as a standard (9) for the ESR study of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ .

The electron spin resonance spectrum of  $\text{La}_2\text{CuO}_4$  ( $\nu_0 = 9.464\text{GHz}$ , room temperature) is shown in Fig. 3(a). The spectrum can be interpreted with

$$g_{\parallel} = 2.310 \pm 0.002, \quad g_{\perp} = 2.062 \pm 0.002,$$

$$A_{\parallel} = (132 \pm 2) \times 10^{-4} \text{cm}^{-1}, \quad \text{and } A_{\perp} = (21 \pm 2) \times 10^{-4} \text{cm}^{-1}.$$

Such parameters are typical of  $\text{Cu(II)}$  in a square planar or tetragonally distorted octahedral site. ESR spectra of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  show a feature with the same  $g$ -value as the perpendicular features seen in the  $\text{La}_2\text{CuO}_4$  spectrum. However, the size of this resonance decreases with sample purification and appears to be due to a trace of the  $\text{La}_2\text{CuO}_4$  phase. The

spectrum of one such sample, shown in Fig. 3(b) (same experimental conditions as the spectrum of Fig. 3(a)) has an intensity about 1% that of pure  $\text{La}_2\text{CuO}_4$ . This fact means that only about 1% of the copper atoms in the  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  heated at  $970^\circ\text{C}$  for 120 hours are in the  $\text{Cu(II)}$  state. Considering that copper in  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  has an average valence of 2.0, it is proposed that the copper has disproportionated into  $\text{Cu(I)}$  and  $\text{Cu(III)}$ .  $\text{Cu(II)}$  is generally the most stable copper ion; therefore, the disproportionation is a unique characteristic of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ . This unique property is probably related to the observed superconductivity at high temperature.

The magnetic susceptibility of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  is plotted against temperature in Fig. 4. The absence of any temperature dependence demonstrates Pauli paramagnetism over the temperature range from 77 to 300 K.  $\text{Cu(II)}$   $3d^9$  electrons are usually localized and characterized by Curie-Weiss behavior; such results were obtained by Ganguly and Rao for  $\text{La}_2\text{CuO}_4$  (10). Since the Pauli-paramagnetic behavior of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  is consistent with delocalized electrons, this would also indicate a high probability for the existence of  $\text{Cu(I)}$   $\text{Cu(III)}$  formed as a result of disproportionation of  $\text{Cu(II)}$ .

Acknowledgement - This research was partially supported by the Office of Naval Research and the authors express their appreciation to the National Science Foundation, Grant No. DMR-820-3667 for the partial support of K. Dwight and to Brown University's Materials Research Laboratory which is supported by the National Science Foundation.

### References

1. C.N.R.Rao and P.Ganguly, Current Science, 56(2), 47 (1987).
2. J. G. Bednorz, K. A. Muller, and M. Takashige, Science, 236, 73 (1987).
3. R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett., 58(4), 408 (1987).
4. J.G. Bednorz, M. Takashige and K. A. Muller. To be published.
5. H.H. Wang, U. Geiser, R. J. Thorn, K. D. Carlson, M. A. Beno, M. R. Monaghan, T. J. Allen, R. B. Proksch, D. L. Stupka, W. K. Kwok, G. W. Crabtree, J. M. Williams, Inorg. Chem., 26, 1190 (1987).
6. P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, D. W. Murphy. To be published.
7. B. Morris and A. Wold, Rev. Sci. Instrum., 39, 1937 (1968).
8. J. M. Long and P. M. Raccah, J. Solid State Chem., 6, 526 (1973).
9. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions." Clarendon Press, Oxford (1970).
10. P. Ganguly and C.N.R. Rao, J. Solid State Chem., 53, 193 (1984).

### Figure Captions

Fig. 1. X-ray diffraction patterns of (a)  $\text{La}_2\text{CuO}_4$ , (b)  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ , (c) reduction products of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ .

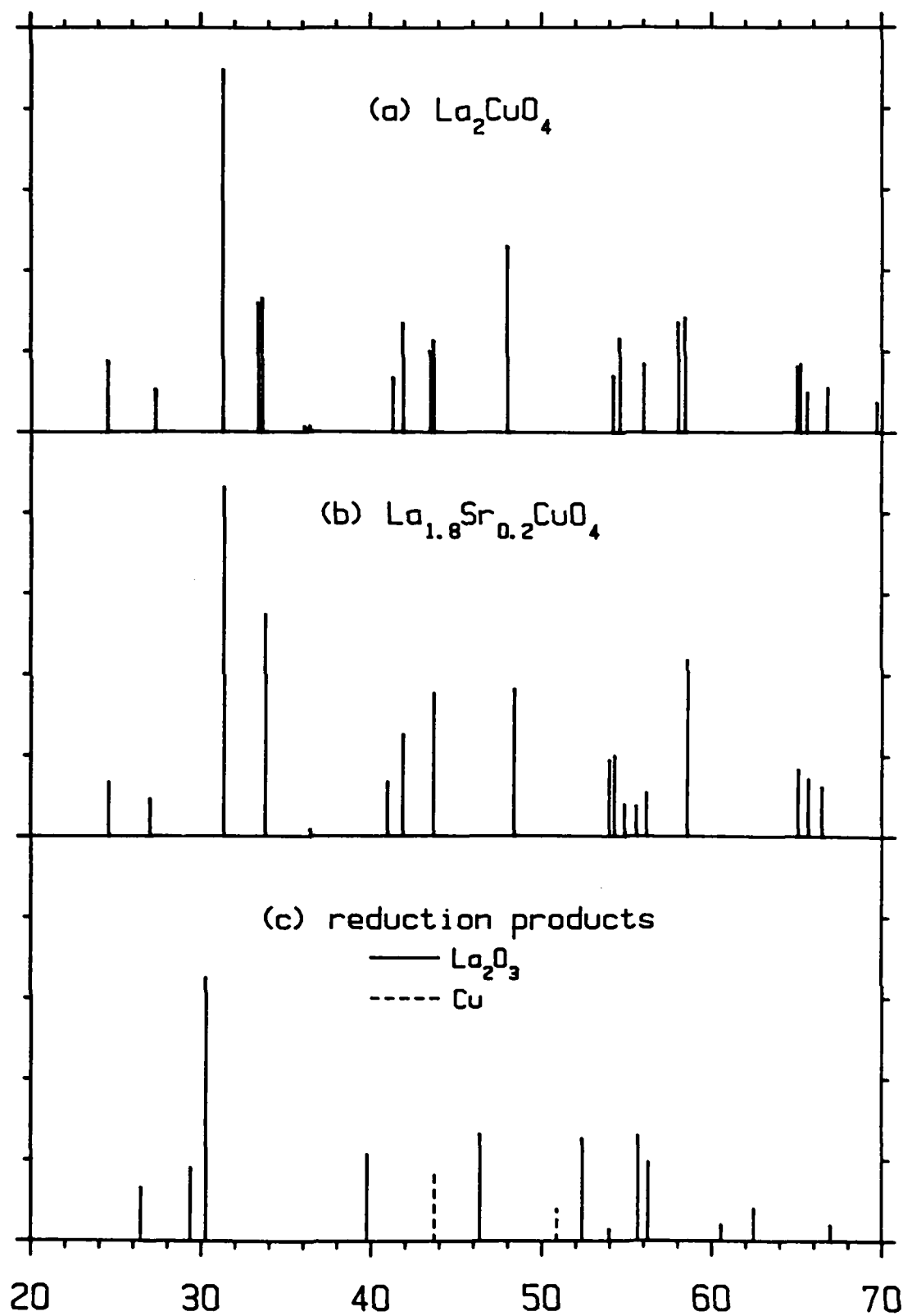
Fig. 2. Temperature programmed reduction profile of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$  in 85%Ar/15%H<sub>2</sub>.

Fig. 3. X-band ESR spectra of (a)  $\text{La}_2\text{CuO}_4$  and (b)  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ . (Microwave power, 200 mW, field modulation amplitude, 1 Gauss.)

Fig. 4. Temperature dependence of the magnetic susceptibility of  $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$ .

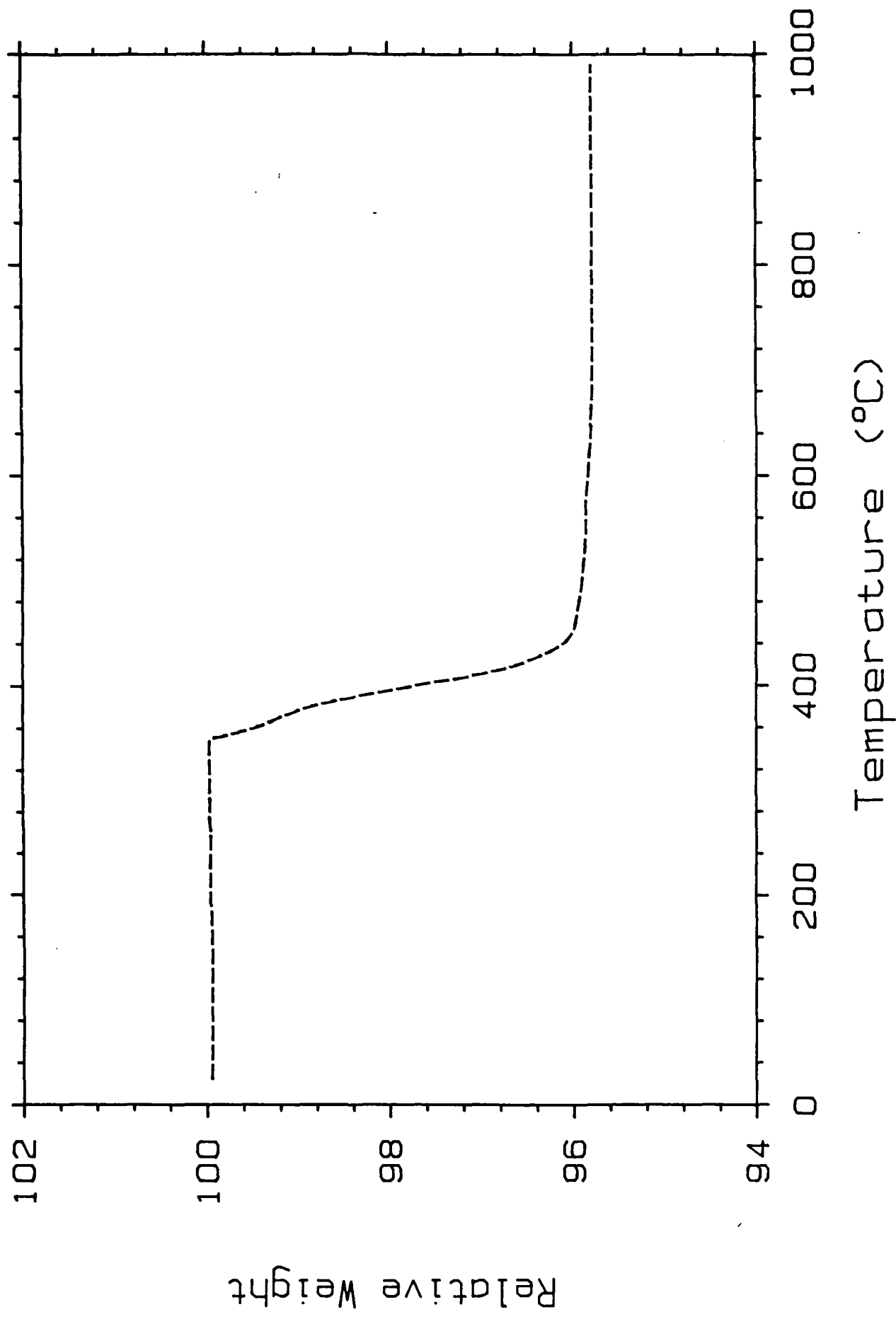
# X-ray Analysis

Relative Intensity

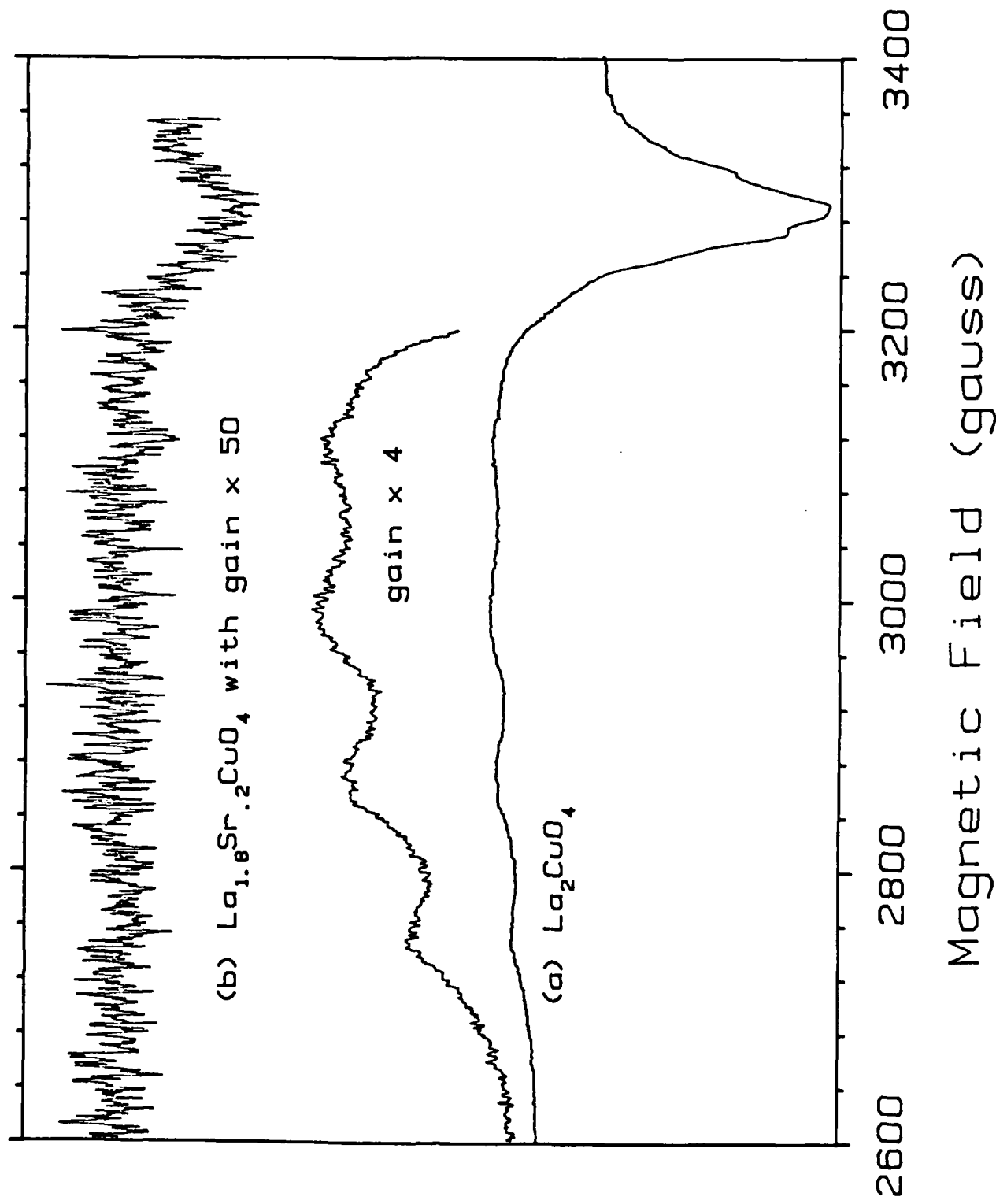


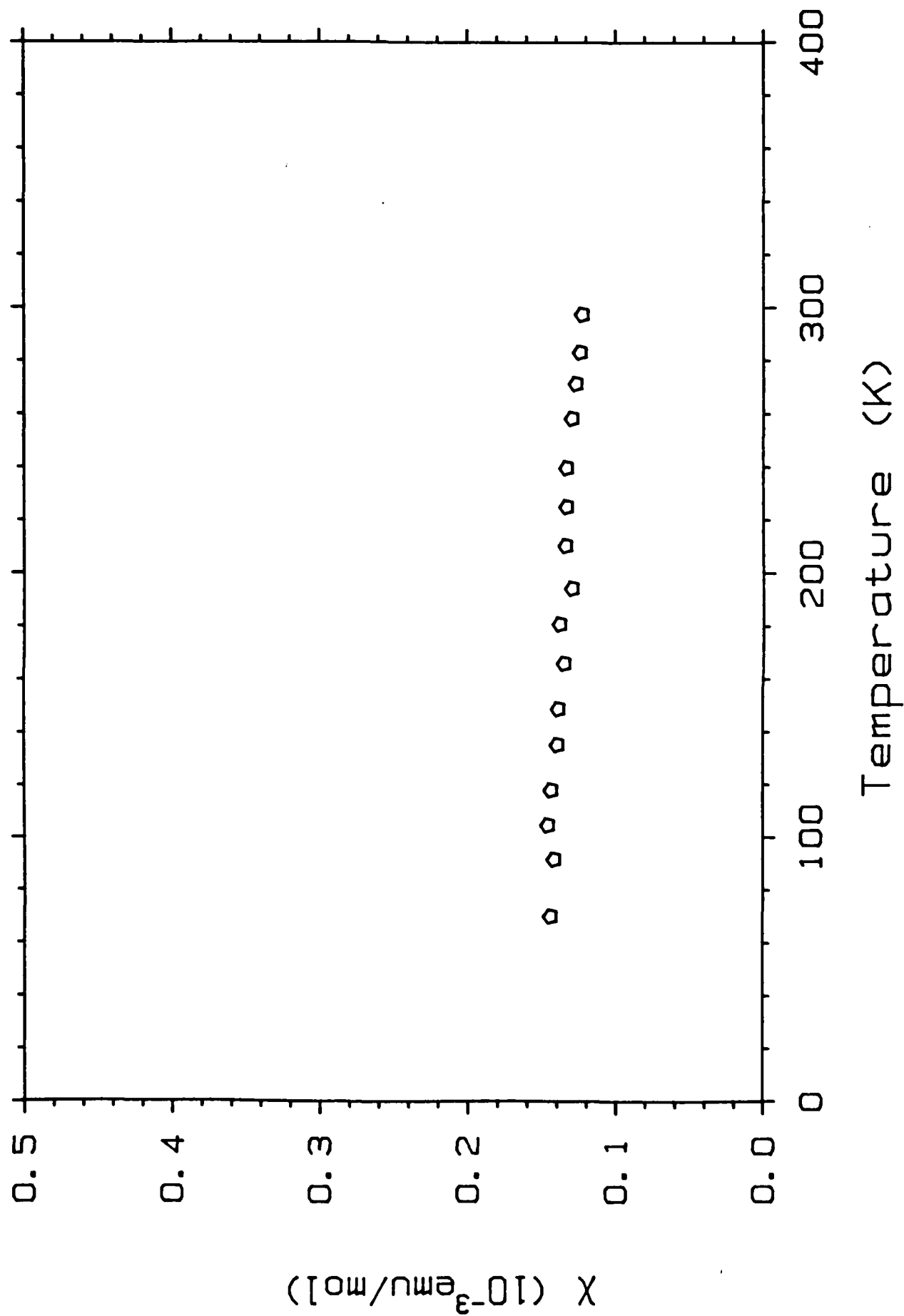
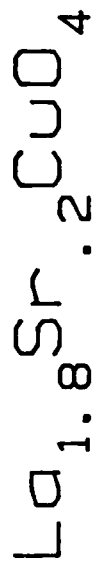
Diffraction Angle  $2\theta$  (deg)

# TPR of $\text{La}_{1.8}\text{Sr}_{.2}\text{CuO}_4$



# ESR of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$







END

8-87

DTIC